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High resolution inelastic scattering of X-rays from bound electrons

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Abstract : Some recent resolution inelastic X-ray scattering experiments on bound electrons are reviewed. Included are X-ray absorption edge fine structure, resonant Raman scattering and Compton scattering. Examples and future trends, based mainly on the use of synchrotron radiation are given.

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1. Scattering cross section

The interaction between the incident photon and the target electron is usually included as a perturbation in the atomic system. If the electron spin term is excluded, this leads to the well-known additional factor H' in the Hamiltonian

$$H' = \frac{e}{mc} \boldsymbol{p} \cdot \boldsymbol{A} + \frac{e^2}{2mc^2} \boldsymbol{A} \cdot \boldsymbol{A}, \tag{1}$$

where $\boldsymbol{p}$ is the electron momentum and $\boldsymbol{A}$ is the vector potential of the electromagnetic field. If $\boldsymbol{A}$ is expressed in terms of the creation and annihilation operators a and a^+, it is obvious that the term involving $\boldsymbol{p} \cdot \boldsymbol{A}$ cannot contribute to the scattering because the number of photons do not conserve. A second order process is, however possible. In the first stage a hole is created (photon annihilation), and then this hole is filled to create a new photon. Under normal conditions (the incident photon energy is larger the electron binding energy), this process is called fluorescence. The resonant term, which dominates the differential scattering cross section at photon energies close to the inner-shell electron binding edge is in dipole approximation for a KL-transition [1]

$$\frac{d\sigma}{d\omega_2} = \frac{r_0^2}{4} \frac{\omega_2}{\omega_1} \frac{\Omega_{KL}(\Omega_{KL} + \omega) gKL}{\hbar \left(\Omega_{KL} - \omega_2\right)^2 + \Gamma_K^2 / 4\hbar^2} \left(\frac{dgK}{d\varepsilon}\right)_\varepsilon, \tag{2}$$

where r_0 is the classical electron radius, ω_1 and ω_2 the angular frequencies of the incident and scattered photons, $\hbar\omega_{KL}$ the KL-fluorescence energy, ε the energy of the ejected photoelectron and Γ_K the life time width of the K-shell energy. The oscillator strength of the KL transition is given by gKL and $\left(\frac{dgk}{d\varepsilon}\right)$ is the oscillator density corresponding transition to the final electron states.

The total cross section can be obtained by integrating eq. (2) over the positive values of the photoelectron kinetic energy ε. Because this cross section is sensitive to the allowed final states, two kind of important information is obtained if the cross section is measured as a function of the incident photon energy across the inner-shell electron binding edge. (i) Just above the edge the allowed states in a solid depend on the band structure and are also affected by the selection rules (1s electrons can only go to the p-like final states etc. in the dipole approximation). This corresponds closely the case in the XANES (X-ray Absorption Near Edge Structure) studies in absorption spectroscopy and, as shown later, combined with a high resolution fluorescence detection it provides information not seen in conventional XANES. (ii) The structure seen in extended region above the absorption edge is usually called EXAFS (Extended X-ray Absorption Fine Structure) and like in the case of XANES it also modifies the fluorescence cross section. EXAFS is due to the scattering of the photoelectrons from the surrounding atoms and the method is widely adapted by a wide range of scientists to study the local environment of an particular atom.

It was found in 1970's [2] that the cross section leading to X-ray fluorescence gives contribution even when the incident photon energy is below the absorption edge. The effect was called resonant Raman scattering (RRS), and it was explained through a virtual hole in the intermediate stage of the second order scattering process. The integrated cross section turns out to be for a KL-transition [3]

$$\left.\frac{d\sigma}{d\Omega}\right)_{KL} = \frac{\Omega_K + \bar{\varepsilon}}{4\pi^2\omega_1}\sigma_K\left(\Omega_K + \bar{\varepsilon}\right)\tan^{-1}\frac{\Gamma_K/2}{\Delta E} \tag{3}$$

providing the energy given to the ejected electron is large enough to neglect the near edge effect. In eq. (3) Ω_K is the K-shell binding energy, $\bar{\varepsilon}$ the average energy of the ejected electron, σ_K the K-shell contribution to the photoelectric absorption and ΔE the incident photon energy relative to the absorption edge.

The second term eq. (1) is usually related to scattering and in the case of inelastic scattering the differential cross section is usually written

$$\frac{d^2\sigma}{d\Omega d\omega} = \left(\frac{d\sigma}{d\Omega}\right)_{Th} S(\boldsymbol{k}, \omega), \tag{4}$$

where ω and $\boldsymbol{k}$ are related to the energy transfer and to the momentum transfer in the scattering process, $(d\sigma/d\omega)_{Th}$ is the Thomson cross section and S is the inelastic scattering

factor. In the case of large momentum transfer the inelastic scattering factor can be written in terms of the electron momentum distribution $n(\boldsymbol{p})$ by defining a quantity called Compton profile $J(p_z)$

$$J(p_z) = \iint dp_x dp_y n(\boldsymbol{p}). \tag{5}$$

Compton profile can also be factorized from inelastic scattering spectrum. This technique, called Compton scattering has been mainly used to study the valence electron properties but also some features related to the bound electrons have been recently utilized.

2. Fluorescence XANES and EXAFS

The standard way to measure the XANES and EXAFS structure using fluorescence technique has been based on a monochromatic (within 1 eV) X-ray beam from a synchrotron source which has been scanned through the absorption edge and the fluorescence signal has been measured with a solid state detector. Despite of the very intensive beam, no tries to improve the beam resolution and thus to see the edge structure with more details, have been done until very recently. This is due to the fact that the natural lifetime broadening of the inner-shell is already of the order of electron volts for K- and L-shells in most materials in these type of studies. Because the inner-shell hole is the intermediate stages this second order process, the lifetime is involved as a convolving factor and the resolution of 1 eV has been appropriate.

This problem was solved in the pioneering work of Hämalàinen and coworkers [4] who used a high resolution spherical crystal spectrometer to monitor the fluorescence intensity. They measured the L_{III} edge of dysprosium, which has the atomic shell energy width of 4.2 eV with an analyzer resolution of 0.3 eV and found a detailed structure in the XANES spectrum, totally invisible in the conventionally measured spectrum. They also succeeded to analyze in detail the differences in dysprosium compounds in terms of the sensitivity of the $5d$ states to the chemical chances. This opens a whole new world in absorption edge studies, it can be applied to EXAFS as well, although the extended range experiment fine steps is significantly more time consuming than conventional EXAFS.

3. Resonant Raman scattering

Although RRS is governed by the same cross section as fluorescence, the presence of the virtual intermediate state causes the share of the available energy between the outgoing photon ($\hbar\omega_2$) and the ejected electron (ε). This can be seen in the energy equation

$$\hbar\omega_2 = \hbar\omega_1 - E_{\text{bind}}(2p) - \varepsilon \tag{6}$$

in the case of KL-resonance (intermediate hole in the K-shell, filled according to the selection rules by $2p$ electron). Apparently $\hbar\omega_2$ (max) is obtained when $\varepsilon = 0$. This can be seen as a sharp edge in the scattered spectrum.

An important application of RRS for atomic inner shell studies is based on eq. (3). If the RRS cross section is measured as function of the incident energy below the desired absorption edge, the inner-shell line width Γ can be determined as a value, which in $(d\sigma/d\Omega)$-$\tan^{-1}$-plot gives a straight line. Hämäläinen and coworkers applied this technique to determine the line widths for Cu and Zn K-shells and for HoL$_{III}$-shell [3] and later for Yb and Ta L_{III}-shells [5] using synchrotron radiation. Compared with the other type of lifetime experiments, which more or less are based on the widths of the fluorescence lines, this method is much easier, and no high resolution spectrometer is required.

It is also possible to measure the double differential cross section of RRS, *i.e.* the scattered spectral distribution. Because it is modified with the final electron state effects, the XANES and EXAFS structures are present. It turns out that unlike in the usual XANES or EXAFS, the inner-shell energy width is no longer a convolving factor, and better resolution can be achieved. Also the edge occurs at the energy determined by the incident energy minus the outer shell energy (see eq. (6)) which makes this kind of experiments more useful in the case of lighter atoms. On the other hand there are always at least two overlapping edges (K-shell hole can be filled by $2p_{1/2}$ and $2p_{3/2}$ electrons etc.) leading to the separation of the contributions. Eteläniemi and coworkers [6] demonstrated the potential of this technique using conventional X-ray tube to measure the XANES spectrum of HoL$_{III}$-edge.

4. Compton scattering

The Compton profile, defined in eq. (5), gives projection of the electron momentum distribution into the scattering vector (direction z in eq. (5)). This relationship is valid providing that the energy given to the electron in the scattering process is large compared with the binding energy [7]. If this is not true, the binding edge of an inner-shell electron can be seen in the Compton profile. This edge occurs at the energy of $\hbar\omega_1 - E_{bind}$ and the contribution of the inner-shell electron to the scattered spectrum is on the low energy side of the edge. Because the possible electron states, available for the ejected electron, are again determined by the band structure and the local atomic configuration, the XANES and EXAFS modulation can be seen in the inner-shell contribution. This is particularly useful in the case of lower elements because the edge energies are too low to be studied with the conventional XANES of EXAFS. For example in the case of beryllium, the K-edge energy is 188 eV, too low to be used in a transmission experiment and also strongly absorbing in the sample leading to surface information only. On the other hand by using a 10 keV radiation, the K-edge occurs at the energy of 9.812 keV which is easily observed and analyzed with high resolution in the Compton profile. The disadvantage of this technique is the small cross section compared with the photoelectric absorption, but this will soon be solved when the next generation synchrotrons are operating.

This kind of technique has been applied to XANES studies by Schülke and coworkers [8], who studied the near edge structure of graphite using synchrotron radiation. The details

related to π- and σ-bonds were nicely seen in their data. Manninen and Hämäläinen [9] measured the K-edge of rhombohedral boron using the high resolution spectrometer at the Brookhaven National Laboratory. The observed XANES structure showed a 20 eV broad band with a peak at 4 eV above the edge, which could be connected to the antibonding πp-states in the B_{12} cluster of the complicated 105-atom unit cell of boron.

Tohji and Udagawa [10] have applied Compton scattering spectroscopy to EXAFS studies. They measured the extended edge structure of graphite and diamond and produced the local atomic coordination including bond lengths in these solids.

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